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Photochemistry at corrugated thin metal films: a phenomenological approach

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ABSTRACT

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A phenomenological model is adopted to explore possible novel photochemical phenomena for molecules in the vicinity of a corrugated thin metal film, with detailed results worked out for the photoabsorption cross section for molecules in the vicinity of a grating film. A mechanism is proposed by which enhanced selective photoabsorption may be achieved based on the different nature of the coupling of the molecular dipole and the incident laser light to the surface plasmon modes of the thin films.

1. INTRODUCTION

The discovery of the dramatic surface-enhanced Raman scattering<sup>1</sup> has opened up the possibility of enhancing other photochemical processes by similar mechanisms employing the resonance condition of the surface plasmon field. Upon realizing the importance of surface roughness in these processes, intensive theoretical<sup>2,3</sup> and experimental<sup>4,5</sup> efforts have been devoted to the study of processes like photoabsorption/dissociation (direct dissociation) of molecules in the presence of both localized<sup>2</sup> and extended<sup>3</sup> surface structures. By now, it has become clear that for such first-order processes, the surface-enhanced field and the induced decay rate will play the role of two competing factors in determining the ultimate enhancement of the process.<sup>2-4</sup>

In this work, we would like to explore the possibility of novel photochemical phenomena for molecules located in the vicinity of a thin metal film. Roughly speaking, when the thickness is thin enough, a thin-film system can be viewed as two surfaces interferring with each other, and hence we would expect richer proximity effects to arise. In the following, we shall study photoabsorption for these molecules by generalizing two of our previous works on photoabsorption<sup>3</sup> and decay rates<sup>6</sup> for the case of a single roughened surface.

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## 2. PHOTOABSORPTION CROSS SECTION

The configuration of our problem is depicted in Fig. 1, where we consider a two-level system (modeled by a dipole moment  $\vec{\mu}$ ) located at  $z = d$  above a thin

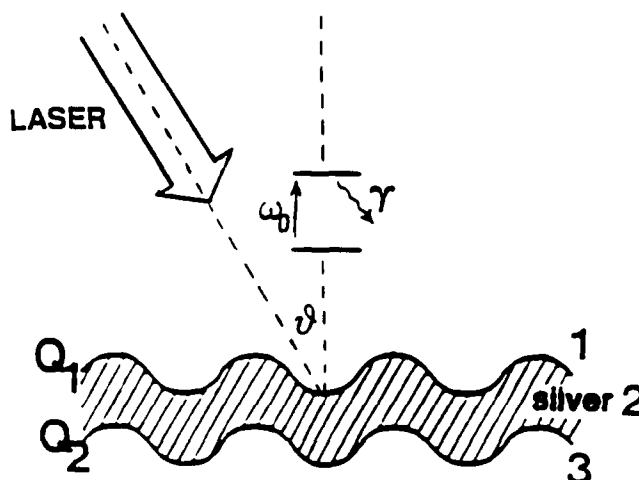


Figure 1. Configuration of the photoabsorption problem at a corrugated thin film.

metal (taken as Ag) film bounded by two grating surfaces located at  $z = 0$  and  $z = t$ , respectively. Thus the profile functions take the simple forms

$$\zeta_1 = \zeta_{o1} e^{iQ_1 x}, \quad \zeta_2 = \zeta_{o2} e^{iQ_2 x}, \quad (1)$$

respectively, where we shall assume small corrugations ( $\zeta_{o_i} Q_i \ll 1$ ), so that perturbation theory can be applied. For simplicity, we consider only replicated films for which  $\zeta_{o1} = \zeta_{o2} = \zeta_o$  and  $Q_1 = Q_2 = Q_o$ , although different combinations of  $\zeta_1$  and  $\zeta_2$  can also yield film systems of great interest.<sup>7</sup> The optical properties of the three media are described by their dielectric functions  $\epsilon_1$ ,  $\epsilon_2 = \epsilon'(\omega) + i\epsilon''(\omega)$  and  $\epsilon_3$ , respectively. Consider p-polarized laser light of the form

$$\vec{E}_{in} = (E_{ox} \hat{e}_x + E_{oz} \hat{e}_z) e^{i(k_z^{(0)} z - \omega t)} e^{i\vec{k}_{||}^{(0)} \cdot \vec{r}_{||}} \quad (2)$$

$$= \vec{E}_o(\omega|z) e^{i\vec{k}_{||}^{(0)} \cdot \vec{r}_{||}},$$

$$\vec{k}_{||}^{(0)} = k_x^{(0)} \hat{e}_x, \quad \vec{r}_{||} = (x, y), \quad (3)$$

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being incident on the system at an angle  $\theta$  with the normal direction. We want to calculate the absorption cross section of the molecule. For simplicity, let us assume that the dipole  $\vec{\mu}$  is oriented perpendicular ( $\vec{\mu} = \mu \hat{e}_z$ ) to the film.

According to the phenomenological model,<sup>2,3</sup> the absorption cross section for the free-molecule case can be obtained in a Lorentzian form as

$$\sigma_o(\omega) = A |\vec{E}_{in}|^2 \sin^2 \theta \frac{\gamma_M^o}{(\omega - \omega_M^o)^2 + (\gamma_M^o/2)^2} \quad (4)$$

where A is a proportionality constant, and  $\omega_M^o$  and  $\gamma_M^o$  denote the natural frequency and the width of the excited state for the free molecule, respectively. In the presence of the substrate film, Eq. (4) then becomes

$$\sigma(\omega) = A |E_z^{dr}(d, \omega)|^2 \frac{\gamma_M}{(\omega - \omega_M)^2 + (\gamma_M/2)^2} \quad (5)$$

where  $E_z^{dr}(d, \omega)$  is now the total field driving the dipole, and  $\omega_M$  and  $\gamma_M$  denote the dressed values for the frequency and width, respectively, due to the presence of the film substrate. Since these are usually dependent on the driving frequency  $\omega$ , Eq. (3) is in general distorted from a Lorentzian shape. Moreover, it is known that the induced frequency shift can most of the time be neglected compared to the induced decay rate,<sup>8</sup> and hence in the following we shall assume  $\omega_M \approx \omega_M^o$  and take into account only the substrate-induced decay rate which can be obtained as

$$\frac{\gamma_M}{\gamma_M^o} = 1 + \frac{3q\epsilon_1}{2k_1^3} \text{Im}G(\omega) \quad (6)$$

where

$$G(\omega) = \frac{E^r(d, \omega)}{\mu} \quad (7)$$

$q$  is the quantum yield of the emitting state,  $k_1$  ( $= \frac{\sqrt{\epsilon_1} \omega}{c}$ ) is the emission wave number, and  $E^r(d, \omega)$  is the reflected field from the film upon incidence by the dipole emissions, acting back on the dipole. Our remaining job then is to calculate the fields  $E^{dr}$  and  $E^r$ .

### 3. SURFACE ELECTROMAGNETIC FIELDS

In order to calculate the surface fields generated by the incident laser field ( $E^{dr}$ ) in Eq. (5) and the dynamic reflected field at the dipole site in Eq. (7), we resort to a perturbative approach formulated by Maradudin and Mills.<sup>9</sup> According to their theory, the  $\mu$ -th theory component for the roughness contribution ( $E^{Ro}$ ) to the reflected field from first-order perturbation theory can be obtained as

$$E_{\mu}^{Ro}(\vec{r};\omega) = - \frac{k^2}{16\pi^3} \int d^2k_{\parallel} e^{i\vec{k}_{\parallel} \cdot \vec{r}_{\parallel}} \int dz' d_{\mu\nu}(\vec{k}_{\parallel}|\omega|zz') \{ [\epsilon_2 \theta(z'+t) - \epsilon_1] \delta(z') \\ \times \hat{f}(\vec{k}_{\parallel} - \vec{k}_{\parallel}^{(0)}) + [\epsilon_3 - \epsilon_2 \theta(-z')] \delta(z'+t) [\hat{f}(\vec{k}_{\parallel} - \vec{k}_{\parallel}^{(0)}) + t] \} \\ \times E_{\nu}^{(0)}(\vec{k}_{\parallel}^{(0)}|\omega|z'), \quad (8)$$

where  $\parallel$  denotes any vector on the xy-plane,  $\hat{f}$  is the Fourier transform of the profile function,  $\theta$  is the Heaviside step function, and  $d_{\mu\nu}$  is the Fourier transform of the two-dimensional "flat propagator" obtained in Ref. 9.  $E_{\nu}^{(0)}$  in Eq. (8) denotes the total field for the homogeneous case of a perfectly flat film. Hence, to calculate  $E^{dr}$ , one simply employs the expressions of  $E_{\nu}^{(0)}$  for a flat film which are available in the literature.<sup>10</sup> Similarly, for the calculation of  $E^r$ , the problem of  $E_{\nu}^{(0)}$  has also been solved by Chance, Prock and Silbey in terms of the Green dyadics.<sup>8</sup> Furthermore, we remark that to evaluate the integral of  $\delta(z')$  in Eq. (8), where  $E_{\nu}^{(0)}$  may be discontinuous across the boundaries of the film, one must adopt Agarwal's modifications and not just take the mean value of the integrals at each side of the boundary.<sup>6,11</sup> Using the various appropriate  $E^{(0)}$ 's, we finally obtain<sup>12</sup>

$$E_z^{dr}(d,\omega) = (1 + R e^{2ik_1 d}) E_{in} \sin\theta + E_z^{Ro}(d,\omega) e^{ik_1 d}, \quad (9)$$

where  $R$  is the Fresnel reflectance for a flat film,<sup>10</sup> and  $E_z^{Ro}$  is given by

$$E_z^{Ro}(d,\omega) = - \frac{k^2}{4\pi} \zeta_0 \{ (\epsilon_2 - \epsilon_1) [C_1 C_2 E_x^{(0)}(\omega|0_+) + C_4 E_z^{(0)}(\omega|0_+)] \\ + (\epsilon_3 - \epsilon_2) [C_1 C_3 E_x^{(0)}(\omega|-t_-) + C_5 E_z^{(0)}(\omega|-t_-)] \} e^{i\alpha_1 d}, \quad (10)$$

where  $k = \omega/c$  and  $E_x^{(0)}$ ,  $E_z^{(0)}$  and  $\alpha_1$  are given in detail in Ref. 12. Similarly, we have<sup>7</sup>

$$E^r(d, \omega) = \frac{i\mu}{\epsilon_1} \int_0^\infty d\lambda \frac{\lambda^3}{h_1} (f_1 - 1) e^{2ih_1 d} + E_z^{Ro'}(d, \omega) \quad (11)$$

where

$$E_z^{Ro'}(d; \omega) = -\frac{k^2}{4\pi} \epsilon_0 [(\epsilon_2 - \epsilon_1) I_1 + (\epsilon_3 - \epsilon_2) I_2] \quad (12)$$

with the functions  $f_1$  and  $h_1$  given in Ref. 7. In Eqs. (10) and (12), the coefficients  $C_i$  and the integrals  $I_i$  are complicated functions of the film parameters and are given in detail in Refs. 12 and 7. Hence, from Eqs. (6), (7), (11) and (12), we then obtain the complete determination of  $\gamma_M$  in terms of  $\gamma_M^0$ . Taking this value for  $\gamma_M$  and together with Eq. (9) into Eq. (5), we can then calculate the photoabsorption cross section at the grating film  $[\sigma(\omega)]$  for a given free-molecule cross section  $\sigma_0(\omega)$ .

#### 4. POSSIBILITY OF ENHANCED SELECTIVE PHOTOABSORPTION

Instead of showing some straightforward model calculation based on Eqs. (4) and (5), here we shall pay attention to a very interesting feature of the problem which may lead to the realization of a mechanism for enhanced selective photoabsorption for adsorbed molecules. In a recent study,<sup>7</sup> we have pointed out that the coupling of the molecular fluorescence radiation to the two thin-film surface plasmons is governed by very different dispersion relations as compared to those in the case of plane-wave light-scattering experiments. The difference arises from the dipole nature of the molecular emission which consists of a superposition of all the plane-wave harmonics. Hence the resonance peaks due to the cross-coupling of the plasmons on the two film surfaces into the long-(and short-)range surface plasmons [L(S)RSP] in the decay-rate spectrum are in general at different positions as compared to those in the light scattering spectrum.<sup>12</sup> Since these peak positions (in both spectra) are very sensitive to the geometrical (roughness, thickness,...) and dielectric properties of the film, for a given level  $\omega_M^0$  one can then try to adjust these parameters so that the cross-coupling peak of the scattered field lies close to  $\omega_M^0$  and that of the induced decay rate stays away from  $\omega_M^0$ . Upon optimal conditions, enhanced selective photoabsorption of this particular level ( $\omega_M^0$ ) may be achieved since the other levels close to it may now be damped seriously due to the fact that they can possibly experience large values for the induced decay rates.

As a numerical illustration, we consider a hypothetical molecular system with

two Lorentzian absorption lines  $\omega_M^0$  as shown in Fig. 2. Let this system be located at  $d = 150 \text{ \AA}$  from a supported grating film with  $\epsilon_1 = 1.0$ ,  $\epsilon_3 = 3.6$ ,  $t = 100 \text{ \AA}$  and  $Q = 1.5 \times 10^{-3} \text{ \AA}$ . From previous analyses,<sup>7,12</sup> the peak due to cross-coupling into LRSP is located at  $\omega \sim 1.1 \text{ eV}$ , whereas that for the light-scattering spectrum is at  $\omega \sim 1.6 \text{ eV}$ . Note that at this distance the coupled SRSP almost vanishes and does not play a role in the photoabsorption process. Hence for the system as shown in Fig. 2, we expect that only the one with  $\omega_M^0 \sim 1.5 \text{ eV}$  will be excited and the other one will be suppressed due to the surface-induced damping. Indeed, these effects are manifested in Fig. 3 where we show a plot of  $\sigma(\omega)$ , except that no enhancement of the line at  $1.5 \text{ eV}$  is observed, due to the fact that the corrugation amplitude used in this calculation ( $\zeta_0 \sim 40 \text{ \AA}$ ) is not large enough. We have tried to increase this to go beyond  $100 \text{ \AA}$ , where we do see enhancement, but then the result goes beyond the validity of our present perturbative approach. Nevertheless, the present results do give very strong indications that such enhanced selective photoabsorption may indeed be possible for deeper grating films, where a non-perturbative treatment must be used.

## 5. CONCLUSION

It is well known that due to its monochromaticity and tunability, the laser has found great applications in various selective photochemical processes. Nevertheless, to have the selective absorption enhanced, one requires a highly-intense laser source, which may then lead to multiphoton processes and hence weakens the selectivity in the photoprocess. In this present mechanism that we are proposing, however, we have made use of the fact that the induced decay rate and the enhanced LRSP field have very different resonance structures, and hence excitation of other levels may be suppressed by the enhanced decay rates at their natural frequencies. Hence, we conclude that it is worth pursuing the problem further using a non-perturbative approach to allow large grating amplitudes for the film and to recalculate  $\sigma(\omega)$  for such a system, so that a realistic enhanced selective photoabsorption may be exhibited.

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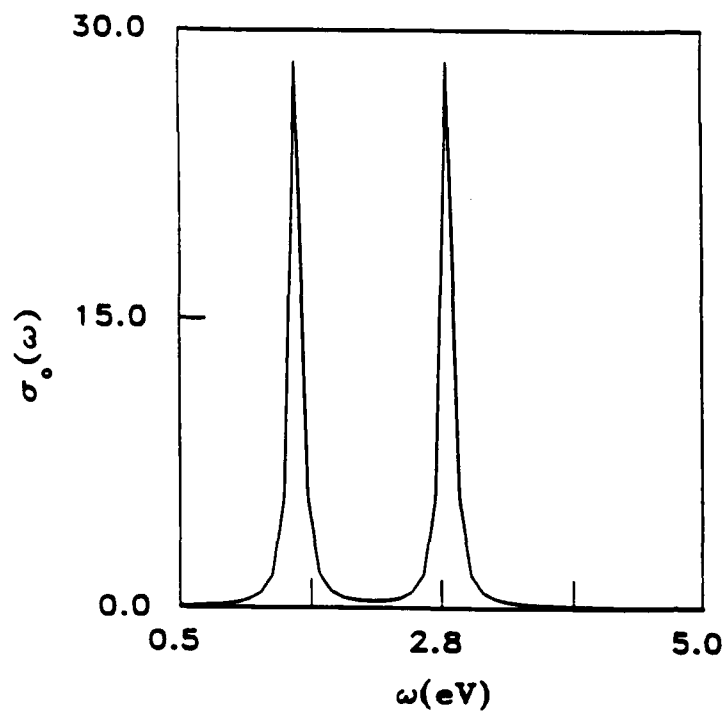


Figure 2. Hypothetical molecular system with two Lorentzian absorption lines.

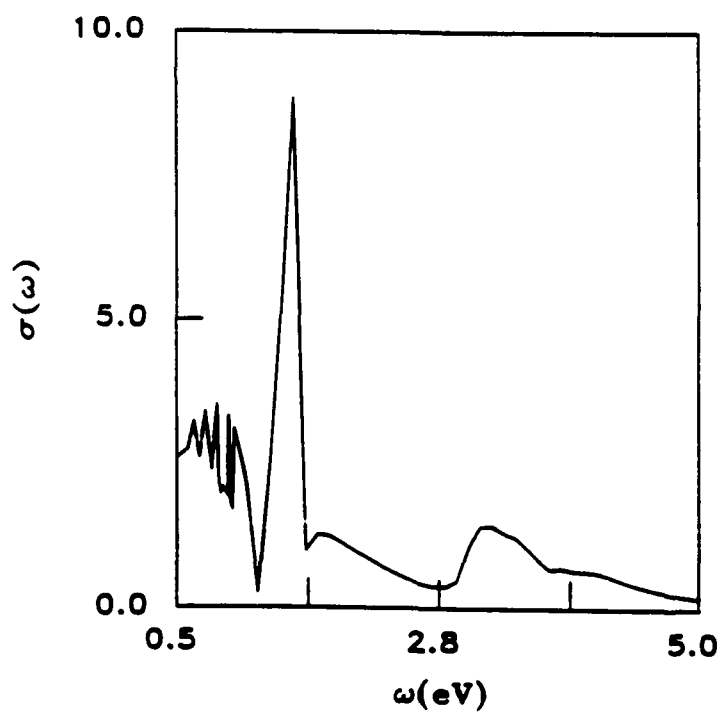


Figure 3. Distorted photoabsorption cross section for the molecular system in Fig. 2 in the presence of a Ag grating film, whose parameters are described in the text.



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